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AN EXPERIMENTAL AND THEORETICAL STUDY OF ANTIKNOCK MATERIALS

DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

WILLIAM HALE CHARCH, B.A., M.A.

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Antiknock Materials

An Experimental and Theoretical Study

The control by chemical means of detonation, as occurring in internal combustion engines, has been studied by Midgley and Boyd,[1,2,3] who have pointed out that certain compounds and elements possess the ability either to suppress or to induce this type of detonation.

Part I of this paper presents the results of an investigation to extend our knowledge as to what class of compounds may function as antiknock materials.

Part II questions the relationship between the suppression of detonation as occurring with acetylene in an open tube and as occurring in motors with motor fuels.

Part III points out the relationship between detonation and the electrical conductivity of the burning gases.

Part IV suggests a chemical theory for the action of antiknock materials, based upon experimental data thus far bearing on the phenomenon.

Part I—Action of Certain Compounds on Detonation

Experimental

TO STUDY the relative effectiveness of antiknock compounds, a one-cylinder, 3/4-kilowatt, Delco light motor was employed. The set-up, including the bouncing pin apparatus, was similar to that described by Midgley and Boyd,[4] and their method of comparison was in general followed.

The antiknock effectiveness of any compound is expressed below by an "antiknock coefficient." It is the inverse ratio of the number of mols of a given compound required to give

[1] *Ind. Eng. Chem.*, **14**, 849 (1922).
[2] *Ibid.*, **15**, 421 (1923).
[3] *Ibid.*, **16**, 893 (1924).
[4] *J. Soc. Automotive Eng.*, **10**, 7 (1922).

the same degree of suppression of detonation as does one mol of lead tetraethyl in a constant volume of the same basic fuel mixture. Lead tetraethyl, the most effective of known antiknock compounds, is given an antiknock coefficient of 100 and all other values are referred to it.

For example, 0.0033 mol of lead tetraethyl and 0.0051 mol of lead tri-*p*-xylyl per liter of fuel were equivalent in their effect in suppressing the knock; hence the antiknock coefficient of lead tri-*p*-xylyl is

$$\frac{Pb(Et)_4}{Pb(Xy)_3} = \frac{0.0033}{0.0051} \times 100 = 64.7$$

This means that the latter compound is molecularly but 64.7 per cent as effective as lead tetraethyl, the standard. This method of comparison serves as a convenient and natural means whereby a number of widely varying results may be compared.

Of the more important solvents employed to carry a compound into solution with kerosene or gasoline for a motor test, there may be mentioned absolute alcohol, amyl alcohol, absolute ether, benzene, xylene, anhydrous pyridine, glacial acetic acid, and various combinations of these. In several instances 3 to 5 per cent emulsions of aqueous solutions were tested. In all cases the compositions of the fuel, containing the compound under examination, were the same throughout the comparison.

Results

Partial results are given in Tables I and II. It has been shown that the antiknock property is exhibited by four elements not included in previous lists.[1] Nickel as the carbonyl was found to have an antiknock coefficient of 30; bismuth in its trialkyl and triaryl derivatives possesses a coefficient of 18.2 to 20.2; cadmium in its alkyl compounds and titanium as the tetrachloride were also found to function, but in a less marked degree. New data are also presented relative to some additional compounds of metals already known to possess antiknock properties.

It had been supposed that the state of valence of the antiknock element was essential in determining which of its compounds should function. Thus, tetravalent lead in its alkyls was known to function as an antiknock, while in its divalent form, as in lead acetate, it was known not to function. That such a generalization, based on valence alone, is not valid became apparent in this work when certain compounds of tetravalent lead, as lead tetrastearate, lead diphenyl di-acetate, etc., were found to be without effect, while certain compounds of divalent lead, as lead thioacetate, were shown to give effective suppression.

Considerable negative evidence was naturally collected. It is reproduced in part here in Table II to give a general idea as to what type of compound was investigated, but

chiefly to serve as an experimental basis from which certain theoretical conclusions are drawn in Part IV.

Part II—Suppression of Detonation in an Open Tube

Midgley and Boyd[2] have described the effect of a small amount of diethyl selenide upon the detonation of acetylene mixtures in an open tube. The detonation of acetylene in the absence of diethyl selenide takes place with a loud, sharp report. However, the presence of this compound in the explosive gases causes a marked suppression of this detonation, observed by the absence of the sharp characteristic "crack" accompanying detonation.

If these phenomena are analogous to detonation and its suppression in the motor, the detonation tube should serve as a convenient instrument whereby the action of antiknock materials could be studied apart from internal combustion engines. The present work attempts to discover what relationships may exist between the action of certain compounds on the two types of detonation.

Table I—Antiknock Compounds

Compound	Formula	Antiknock Coefficient	Method of Preparation
Lead tetraethyl	$Pb(C_2H_5)_4$	100	General Motors Research Corp.
Lead tetraphenyl	$Pb(C_6H_5)_4$	59	*Ber.*, **37**, 1125 (1904)
Lead diethyl dichloride	$Pb(C_2H_5)_2Cl_2$	67	*Ber.*, **49**, 2441 (1916)
Lead diphenyl dimethyl	$Pb(C_6H_5)_2(CH_3)_2$	97	
Lead diphenyl diethyl	$Pb(C_6H_5)_2(C_2H_5)_2$	93.5	
Lead diphenyl dichloride	$Pb(C_6H_5)_2Cl_2$	72 (approx.)	*Ber.*, **20**, 3332 (1887)
Lead diphenyl dibromide	$Pb(C_6H_5)_2Br_2$	60 (approx.)	
Lead diphenyl diiodide	$Pb(C_6H_5)_2I_2$	80	*Ber.*, **20**, 721 (1887)
Lead tri-*p*-xylyl	$Pb(C_8H_9)_2$	64.7	*Ber.*, **52B**, 2165 (1919)
Lead ethyl xanthogenate	$Pb(C_2H_5OCSS)_2$	7.1	$PbAc_2$ + 2EtOCSSNa
Lead thioacetate	$Pb(CH_3COS)_2$	8.4	$PbCO_3$ + $2CH_3COSH$
Bismuth triphenyl	$Bi(C_6H_5)_3$	18.2	*Ber.*, **37**, 4720 (1904)
Bismuth trimethyl	$Bi(CH_3)_3$	20.2	
Bismuth triethyl	$Bi(C_2H_5)_3$	20.2	
Stannic chloride	$SnCl_4$	3.5	Baker's, C. P.
Stannic iodide	SnI_4	12.8	Abegg's Handbuch, **3**, 589
Tin diethyl diiodide	$Sn(C_2H_5)_2I_2$	12.3	Abegg's Handbuch, **3**, 590
Cadmium dimethyl	$Cd(CH_3)_2$	1.05	*Bull. soc. chim. ind.*, **31**, 125 (1922)
Titanium tetrachloride	$TiCl_4$	2.7	Kauffman and Lattimer
Titanium tetraiodide	TiI_4	Over 2.7 (due to iodine content)	Abegg's Handbuch, **3**, 433
Antimony triphenyl diiodide	$Sb(C_6H_5)_2I_2$	(approx.) 4.0	$Sb(C_6H_5)_3$ + I_2
Monophenyl arsine	$AsH_2(C_6H_5)$	Between 1 and 2	*Am. Chem. J.*, **33**, 101 (1905)
Triphenyl arsine	$As(C_6H_5)_3$	(approx.) 1.4	Made at American University
Triphenylmethyl arsonium iodide	$As(C_6H_5)CH_3I$	Between 0.7 and 1.0	$As(C_6H_5)_3$ + MeI
Aluminium ethyl iodide	$Al_2(C_2H_5)_3I_3$	Very weak (due to iodine content)	*Ann. Suppl.*, **4**, 112 (1865–6)

Apparatus

The apparatus used in the present instance included no radical departure from that previously employed by Midgley

and Boyd.[1] An auxiliary tank of such dimensions as to permit its use with hydrogen in a 2:1 ratio with the oxygen of the air was substituted in later experiments for the acetylene tank.

Experimental

The intensity of detonation or the degree of its suppression was in all cases judged by ear. The difference in the nature and the intensity of the reports with and without a suppressing agent were so marked that a more accurate method of observation was unnecessary. Seventy-five to one hundred charges were fired, using any one suppressing agent, alternating between the acetylene-air and acetylene-air-compound mixtures at intervals of every several firings. Care was taken to insure in the explosive gases the presence of very nearly equal molecular quantities of the compounds

Table II—Compounds without Effect in Suppressing the Knock

Compound	Formula	Method of Preparation
Ammonium chloride–lead tetrachloride	$2NH_4Cl.PbCl_4$	Abegg's Handbuch, **3**, 1741
Benzaldehyde lead	$(C_6H_5CHO)_2Pb$	*Helvetica Chim. Acta.*, **5**, 721 (1922)
Lead diphenyl diacetate	$Pb(C_6H_5)_2(C_2H_3O_2)_2$	*Ber.*, **20**, 3332 (1887)
Lead tetrastearate	$Pb(C_{17}H_{35}COO)_4$	*Compt. rend.*, **136**, 1664 (1903)
Lead tetracetate	$Pb(C_2H_3O_2)_4$	*Compt. rend.*, **136**, 675, 891 (1903)
Lead diphenyl dinitrate	$Pb(C_6H_5)_2(NO_3)_2$	*Ber.*, **20**, 3332 (1887)
Lead diphenyl carbazide	$PbC_{13}H_{10}N_4O$	*Compt. rend.*, **130**, 1478 (1901)
Stannic bromide	$SnBr_4$	Abegg's Handbuch, **3**, 589
Zirconium tetrachloride	$ZrCl_4$	Abegg's Handbuch, **3**, 501
Sodium zinc ethyl	$Zn(C_2H_5)_2.NaC_2H_5$	*Ann.*, **111**, 234 (1859)
Gold chloride	$AuCl_3$	Baker's
Tungsten hexachloride	WCl_6	*Chem. News*, **86**, 66 (1904)
Ferric chloride (anhyd.)	$FeCl_3$	Baker's, C. P.
Ferric dimethyl glyoxime	$Fe(C_4H_7N_2O_2)_3$	*Z. anorg. Chem.*, **46**, 157 (1905)
Ferric ethyl xanthogenate	$Fe(C_2H_5OCSS)_3$	$FeCl_3 + 3C_2H_5OCS_2Na$
Aluminium triethyl	$Al(C_2H_5)_3$	*Ann. Suppl.*, **4**, 112 (1865–6)
Aluminium chloride (anhyd.)	$AlCl_3$	Baker's, C. P.
Bismuth triphenyl dichloride	$Bi(C_6H_5)_3Cl_2$	*Ann.*, **251**, 323 (1889)
Bismuth triphenyl dibromide	$Bi(C_6H_5)_3Br_2$	*Ann.*, **251**, 323 (1889)
Dicarbonyl chloroplatinite	$Pt(CO)_2Cl_2$	*J. Chem. Soc.*, **59**, 598 (1891)
Platinic chloride	$PtCl_4$	Baker's
Nickel dimethyl glyoxime	$Ni(C_4H_7N_2O_2)_2$	Precipitation by reagent
Nickel ethyl xanthogenate	$Ni(C_2H_5OCSS)_2$	*Compt. rend.*, **152**, 869 (1911)
Nickel diphenyl carbazide	$NiC_{13}H_{10}N_4O$	*Compt. rend.*, **130**, 1478 (1901)
Copper dimethyl glyoxime	$Cu(C_4H_7N_2O_2)_2$	Precipitation by reagent
Copper diphenyl carbazide	$Cu_2C_{13}H_{10}N_4O$	*Compt. rend.*, **130**, 478 (1901)
Cobalt ethyl xanthogenate	$Co(C_2H_5OCSS)_2$	*Compt. rend.*, **152**, 869 (1911)
Cobalt succinimide	$CoC_8H_8N_2O_4$	*Ber.*, **39**, 2177 (1906)
Mercuric ethyl xanthogenate	$Hg(C_2H_5OCSS)_2$	*Compt. rend.*, **152**, 869 (1911)
Chromium pentaphenyl bromide[a]	$Cr(C_6H_5)_5Br$	*Ber.*, **54**, 1909 (1921)
Zinc ethyl xanthogenate	$Zn(C_2H_5OCSS)_2$	*Compt. rend.*, **152**, 869 (1911)
Nitrogen sulfide	N_4S_4	Bender Erdmann "*Preparationkunde*"
Phenyl carbylamine	C_6H_5NC	*Ann.*, **270**, 274 (1892)
Ethyl carbylamine	C_2H_5NC	*Ann.*, **270**, 274 (1892)

[a] Less than 0.1 per cent by weight of chromium pentaphenyl bromide could be dissolved in a fuel suitable for test. This compound would be expected to exhibit antiknock properties if larger concentrations could be tested. (Theory, Part IV)

tested. This was done in part by regulating the temperature, and consequently the vapor pressure, of the compound picked up by the gases in flowing through the by-pass, and in part by regulating the amount of these gases themselves. Table III compares the effects of a series of compounds upon the detonation of acetylene in an open tube with their effects on the detonation of kerosene in engines.

Table III—Comparison of Effect in Motor and in Open Tube

Compound	In Motor	In Open Tube
Methyl iodide	Suppresses	Suppresses
Ethyl bromide	Induces	Suppresses
Bromine	Induces	Suppresses
Chloroform	Nearly inert	Suppresses
Carbon tetrachloride	Nearly inert	Suppresses
Lead tetraethyl	Suppresses	Suppresses

The apparatus was next used with hydrogen-air mixtures. The explosions took place best in a tube about 1 meter long and of about 30 mm. internal diameter. The effects of the presence of diethyl selenide, methyl iodide, lead tetraethyl, ethyl bromide, ammonia gas, mercury diethyl, and methanol vapors were observed in the manner already described. None of these compounds exerted the slightest effect in suppressing the intensity of the explosion. Diethyl selenide even appeared to increase the loudness of the reports.

Explosion and Detonation

Very little appears in the literature relative to the chemical nature of detonation in engines. The view held here is that it is a sudden disruption of the molecule and thus depends in a large part upon the stability toward heat of the molecule itself. This view is supported by the following facts:

(1) Straight-chain compounds in general are more readily subject to detonation than are ring compounds.

(2) Long-chain hydrocarbons detonate more readily than do the lower members of the same series, which are more stable toward heat.

(3) Analyses of exhaust gases obtained when a motor is knocking show larger percentages of free carbon and free hydrogen resulting from this initial disruption than is the case when the motor is not knocking.

(4) The extremely high and almost instantaneous pressures accompanying detonation suggest the sudden appearance of some chemical phenomena other than simple oxidation, although the latter may take place naturally as an after-burn with the hydrocarbon residues resulting from detonation.

(5) Detonation may take place (as with acetylene and metallic acetylides) in the absence of oxygen and is favored by high temperatures and pressures.

If this conception of detonation is accepted, the only manner in which hydrogen could detonate would be

$$H_2 \rightleftharpoons H + H$$

The fact that the reports with hydrogen in the tube, although very loud, were lacking in the sharp characteristic "crack"

accompanying the detonation of acetylene, indicates that this equation probably does not describe the reaction. The term "explosion," meaning very rapid oxidation, is therefore applied in this instance as distinguished from "detonation," meaning an almost instantaneous disruption of the molecule. Throughout these pages the above meanings are attached to these terms.

Discussion

If the suppression of detonation in the tube with acetylene-air mixtures were strictly comparable to the knock or detonation in engines, compounds which influence the latter phenomena would be expected to affect the former in the same manner. That such is not the case is clear from Table III. In addition to these observations, it should be noted that:

(1) Detonation in engines is dependent upon higher pressures and temperatures than obtain with the tube.

(2) Fuels of widely different chemical characteristics have thus far been used in the two cases.

(3) The shape of the tube and that of the engine cylinder are decidedly different. Furthermore, the engine cylinder is closed on all sides, while one end of the tube is always open to the air.

(4) Even though the detonation of acetylene in the tube and that of kerosene (or gasoline) in the motor may be fundamentally the same phenomenon, it does not follow that compounds which affect it under one set of conditions will do so in precisely the same manner under an entirely different set. It is possible (Part IV) that antiknock compounds may be directly dependent upon the specific conditions prevailing in the motor but absent in the tube, in order to function.

Conclusion

In view of the inconsistent results of Table III and the considerations just enumerated, it is concluded that an attempt to apply the results or observations made with the detonation tube to a study or an explanation of the suppression of the fuel knock in the motor, or vice versa, is unjustified. When the term "antiknock compound" is used here, it has no reference to the apparent suppressing effect of any compound in the tube. This effect is best explained on a basis of its own, rather than to confuse it with the true antiknock effect of certain compounds acting differently under an entirely different set of conditions in the motor.

Part III—Electrical Conductivity of the Cylinder Gases as a Function of Detonation

The following work was undertaken to determine what, if any, relationship exists between gaseous ionization in internal combustion engines during operation and detonation.

Apparatus

The one-cylinder motor referred to in Part I was employed. Figure 1 is a cross-section diagram of a special motor head used in this work. It was designed to accommodate four spark plugs. Plug F was used for firing, while to the electrodes of plugs E and E' were sealed small plates of heavy platinum foil about 0.8 cm. square. The porcelain of the plugs insulates them from the motor. Plug X was blank but permitted a shift in the position of one of the electrodes if desired. B is a battery of eight dry cells, with key K in series. R and R' are resistance boxes and G a very sensitive galvanometer.

Experimental

The motor was allowed to run for at least half an hour in every case before observations were started, so that it could warm up completely and come to constant knocking conditions. The current registered by the galvanometer was never steady, and it was necessary to take the average of the readings at 10-second intervals over a period of several minutes to obtain the mean deflection corresponding to the detonation tendency of the particular fuel employed. The results of two typical sets of observations are recorded in Tables IV and V. Figure 2 reproduces the results of Table V in the form of a curve.

Table IV—Electrical Conductivity of Various Fuels

Fuel	Average deflection Cm.	Knock by Ear
50% Gasoline 50% Kerosene	14.70	Very intense
Gasoline	7.35	Intense
50% Gasoline 50% Benzene	3.20	Moderately loud
30% Gasoline 70% Benzene	1.60	Complete suppression

Table V—Relation between Concentration of Lead Tetraethyl and Electrical Conductivity

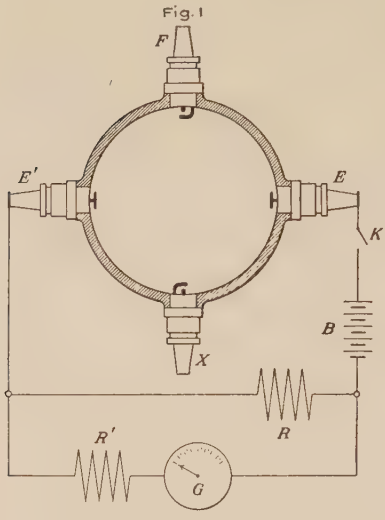
Basic fuel: 50 per cent mixture of gasoline and kerosene to which varying amounts of lead tetraethyl were added

Lead tetraethyl by volume Per cent	Average deflection Cm.	Knock
0.0	14.7	Very intense
0.1	7.4	Intense
0.2	5.6	Moderately loud
0.3	3.6	Barely audible
0.5	1.5	
0.7	1.13	
1.0	0.9	Not audible
2.0	0.5	
4.0	0.5	

Application

The results at once suggest a new method for measuring detonation in internal combustion engines. Midgley and

Boyd[4] mention the four means whereby detonation in internal combustion engines may be measured as (1) listening method, (2) bouncing pin method, (3) temperature method, and (4) indicator method. To this list might be added a fifth, the electrical conductivity method based upon the present observations. The results indicate that there is a direct relationship between the intensity of detonation and the electrical conductivity (or ionization) of the cylinder gases during combustion.



Complete details of this method and the relation of its results to those of other methods were not worked out, owing to the pressing of other lines. Its results, however, recommend it to further investigation. It has the advantage of recording changes in conductivity, both below the range of audible detonation and during intense detonation where the gas volumes of the bouncing pin method are no longer proportional to intensity but begin to approach an asymptote.

Theoretical Discussion

The results show that gaseous ionization decreases with decreasing detonation in internal combustion engines. This decrease is noted irrespective of whether the knock is suppressed by the addition of an antiknock compound (lead tetraethyl), or, by changing the composition of the fuel itself to give one with less tendency to detonate (increasing the percentage of benzene). Thus it appears that antiknock materials affect this ionization only in so far as they tend to suppress detonation, rather than acting *per se* in removing ions from the gases, as has been suggested by Wendt.[5]

If the view of the chemical mechanism of detonation suggested in Part II is adopted, then the increased gaseous ionization present when a fuel is knocking may well be attributed in part to the presence of ions resulting from the sudden disruption of a large number of molecules. It may be also due in part to (1) the presence of highly heated carbon particles;[6] (2) an increase in the ordinary thermal ionization, for it is a matter of common observation that

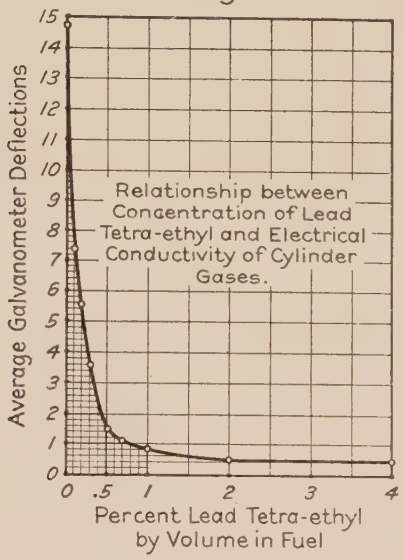
[5] *Ind. Eng. Chem.*, **16**, 890 (1924).

[6] Dickinson, *J. Soc. Automotive Eng.*, **8**, 558 (1921).

knocking is accompanied by an increase in the temperature of the motor; and (3) the increase in ionization resulting from the more rapid rate of oxidation accompanying this rise in temperature.

Any means, therefore, mechanical (as motor design), or chemical (as composition of fuel or presence of antiknock bodies), which would tend to decrease detonation would at the same time decrease this ionization since it either *re-*

Fig. 2



sults from or *accompanies* detonation, rather than causes it in the sense proposed by Wendt.

Part IV—A Chemical Theory of Antiknock Materials and Their Action in Suppressing Detonation

Several theories, of which two may be mentioned here, have been thus far advanced to explain the action of antiknock materials. Midgley[2] has suggested a radiation hypothesis, and Wendt[5] has suggested that the antiknock material, present in advance of the flame front, is an absorber of electrons which are assumed to be the direct cause of detonation.

The theory developed below attacks the problem from an entirely different angle and is based in a large measure on a comparative study of the chemical properties common and peculiar to most antiknock compounds. It thus attempts to define an antiknock material in terms of chemical properties, and then to show how these properties may account for the effect of the compound in suppressing detonation.

Development of the Theory

(A) Volatility—An examination of a list of antiknock compounds (Part I) will at once reveal volatility or at least an appreciable vapor pressure below 400° C., as a common property. Although no direct relationship appears to exist between antiknock effectiveness and volatility alone, it nevertheless is assumed as the first necessary factor in determining that any compound shall function as an antiknock material.

(B) Behavior When Heated—The second characteristic property is best illustrated by a simple test tube experiment. If, for example, a drop of lead tetraethyl or nickel carbonyl be placed in a test tube and heated, it first volatilizes and then as the vapor is further heated a puff occurs usually accompanied by a flash, and there results a deposition of the metal in the form of a very fine black dust. Such compounds when heated in the air decompose directly with liberation of fine particles of the free metal,[7] thus:

$$Ni(CO)_4 \xrightarrow{heat} Ni + 4CO \qquad (I)$$

The reaction has no intermediate stages and is monomolecular. This behavior is characteristic, to some degree at least, of practically all the organo-metallic compounds known to possess antiknock properties, and notably includes those compounds of lead, selenium, tellurium, arsenic, antimony, bismuth, tin, cadmium, and nickel so functioning. The mercury alkyls behave similarly, but exert no antiknock effects. The reason for this will appear later.

As a consequence of this second condition, volatile organometallic compounds of aluminium, zinc, boron, etc., are at once excluded as antiknocks. These compounds undergo, when exposed to the air, spontaneous and complete oxidation even at ordinary temperatures. Thus:

$$M(Et)_2 \xrightarrow{O} M(OEt)_2 \xrightarrow{O} MO + \text{oxidation products} \qquad (II)$$

The rapidity of this reaction is so great that it is completed before any tendency of the compound to decompose when heated in the air according to Reaction I may be realized. Although these compounds when heated in an inert atmosphere may or do decompose according to Reaction I, their failure to do so in the air means that they fail to possess the second property here assumed to be characteristic of an antiknock material, and are at once excluded from playing such a role.

In this connection the special behavior of certain metallic alkyls, such as those of bismuth, cadmium, antimony, and arsenic, should be considered. These compounds on exposure to the air undergo oxidation to a certain extent according to Reaction II, but the action is slower than in the case of the corresponding compounds of zinc, aluminium, phosphorus, and boron. If heated rapidly in the air, they

[7] Mittasch, *Z. physik. Chem.*, **40**, 1 (1902).

do decompose in part with direct liberation of their metal. In such a case Reactions I and II are proceeding simultaneously, as in the case of cadmium dimethyl:

$$Cd(CH_3)_2 \xrightarrow{heat} Cd + C_2H_6 \qquad (I)$$

$$Cd(CH_3)_2 \xrightarrow{O} Cd(OCH)_3 \longrightarrow CdO + \text{oxidation products} \qquad (II)$$

The observed effect of such compounds as antiknocks is thus only a partial effect obtained from that fraction of the total metal present which enters into Reaction I. This would indicate that their effectiveness as antiknocks should be materially greater than that observed, should compounds of these elements be discovered which would show a decreased tendency to react according to Reaction II.

In this particular the facts are in good agreement with the theory. The most effective antiknock compounds are those of lead, selenium, tellurium, and nickel (carbonyl), all of which show little or no tendency to undergo direct oxidation in the air. Moreover, they may be heated in the air with no indication of a reaction until the sudden decomposition occurs which gives practically quantitative deposition of the metal. With the organo-metallic compounds of arsenic, antimony, bismuth, tin, and cadmium, however, the spontaneous tendency to oxidation represented by Reaction II begins to appear in varying degrees, with a consequent decrease in their antiknock efficiency. It should also be noted that this stability of such compounds toward oxygen increases roughly with the atomic weight of the element. The family, arsenic, antimony, and bismuth, with antiknock effectiveness increasing correspondingly, illustrates such a case.

Finally, this property of stability toward oxygen is also one which varies widely from element to element but which remains fairly constant for related compounds of any one element. In so far as this is true it is in harmony with the observation[2] that the antiknock efficiency follows a corresponding relation. Nothing inconsistent with experimental data is thus introduced by conditions (A) and (B).

(C) Influence of Antiknock Metal on Combustion—The anomalous behavior of the mercury alkyls which fulfil conditions (A) and (B) already laid down, but which possess no antiknock properties, has been mentioned. It is clear that, in addition to volatility and mode of decomposition of the compound when heated in the air, there must be another factor which contributes to the antiknock phenomenon if the present line of reasoning is to be followed. The failure of these compounds to function will be clearer when the role played by the fine metallic particles in suppressing detonation is considered.

When the particles of a metal such as lead are liberated in the hot oxidizing atmosphere of the cylinder—for example, by the decomposition of lead tetraethyl—they would tend to undergo almost immediate oxidation. This im-

mediate oxidation of the liberated metallic particles is assumed to be the third condition necessary to the functioning of the antiknock material. It is held that the nature of the oxidation of the antiknock material under the conditions of its operation and the influence of this oxidation upon that of the combustible cylinder gases are sufficient to account for its effect in causing a suppression of detonation of the fuel with which it is used.

The very fine particles (or vapor) of the antiknock metal are conceived as undergoing such rapid oxidation as to develop sufficient heat to raise them momentarily much above the temperature of the yet unburned gases in which they are present. There is thus created at a definite stage in the engine cycle a large number of centers, in and very close about which there is produced an abnormally high temperature. Such a condition would tend to cause a partial oxidation of the fuel rather homogeneously throughout its entire volume. The antiknock would thus function as a kind of auxiliary ignition system, tending to start oxidation of the fuel ahead of the actual flame front in a region of hot, highly compressed gases. These gases under other conditions would be chemically unchanged until the flame front had passed through them, or until their pressure and temperature had become great enough to cause their detonation.

The possibility of starting oxidation in a combustible fuel mixture by means of a hot metallic particle may be more apparent from the following considerations: The preparation of metals in a pyrophoric state is well known. Lead or iron, for example, if sprinkled into the air in this condition will undergo immediate oxidation with incandescence even at ordinary temperatures, indicating, qualitatively at least, that high temperatures are actually developed. To illustrate further, suppose 1 gram molecule of lead oxidizes according to the equation[8]

$$Pb + O \longrightarrow PbO + 50{,}300 \text{ calories}$$

If, as a rough approximation, we assume that the specific heat of lead does not change from its value[9] at 300° C. and that the specific heat of lead oxide is the same as that of lead, then if the heat liberated in the reaction were thought of as raising the temperature of the system, a final temperature of about 5000° C. would be attained.

It is not implied here that such a temperature is actually realized, but it is considered sufficiently apparent that relatively high temperatures may be reached under appropriate conditions. If the size of the particle is extremely small so that the oxidation is practically instantaneous, it is reasonable to suppose that temperatures of the order of 1000° to 2000° C. may be momentarily attained. The

[8] Günther, *Z. Elektrochem.*, **23**, 197 (1917).
[9] Glaser, *Metallurgie*, **1**, 103, 121 (1904).

actual motor conditions under which an antiknock functions favor such a view. Consider lead tetraethyl to be present (about 0.1 per cent by volume) in the cylinder gases. When liberation of the lead takes place, it will tend to yield a mere colloidal dust of particles far smaller than those of pyrophoric metals as ordinarily prepared. Their rapid oxidation with the attainment of localized high temperatures would be further accentuated by the fact that liberation of the particles actually takes place in a motor cylinder in a compressed atmosphere and one already hot.

Consideration of the data for the heats of oxidation and for the specific heats of various metals indicates that temperatures of about the same order as in the case of lead would be developed by the following metals: iron, tin, nickel, cadmium, titanium, bismuth, selenium, tellurium, arsenic, and antimony. However, in the case of particles of platinum, gold, silver, and mercury, because of the comparatively small heats of oxidation (with gold it is negative), the expected temperature would be very much less than with the other metals just mentioned.

Granted the development of high temperatures by the antiknock particles, the probability of starting oxidation of the fuel thereby is in good agreement with data on the spontaneous ignition temperatures of motor fuels. The available data[10] are restated in Table VI.

Table VI—Spontaneous Ignition Temperatures

Fuel	In air ° C.	In oxygen ° C.
Gasoline (Anglo-American Oil Co.)	392	...
Kerosene (Anglo-American Oil Co.)	367	...
Pentane	560 to 570	...
Hexane[10]	...	288
Heptane[10]	...	281

Application of Theory to Motor Conditions

Figures 3 to 7 represent more definitely in a diagrammatic way the part which the antiknock compound plays in the combustion process. Figure 3 represents unchanged and relatively cool fuel, air, and antiknock vapor in the cylinder at the end of the suction stroke. Near the end of the compression stroke (Figure 4) the temperature of the charge has been raised, owing to conduction and adiabatic compression. The spark plug fires the charge just before dead center, and the flame front (Figure 5) begins to travel outward while the piston is traveling downward. Further adiabatic compression of the unburned gases ahead of the flame front continues to raise their temperature. However, by this time (or even before firing) their temperature has become sufficiently high to cause independent decomposition

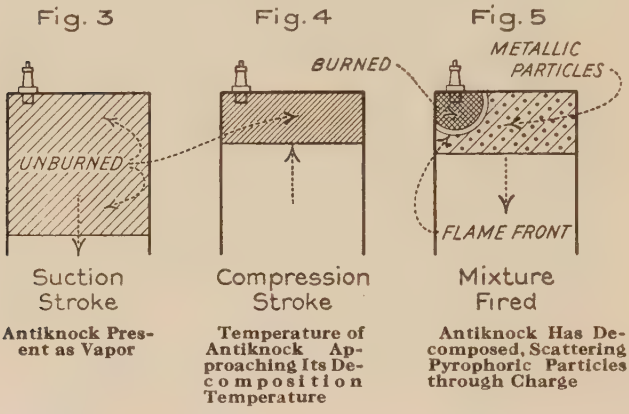
[10] Moore, *J. Soc. Chem. Ind.*, **36**, 109 (1917), states that the spontaneous ignition temperatures decrease with increase in molecular weight, hence the values for hexane and heptane in air would be lower than that of pentane given.

of the antiknock compound (Figure 6) and subsequent oxidation of its particles (or vapor) as:

$$Pb(Et)_4 \longrightarrow Pb + 2C_4H_{10} \qquad (I)$$

$$Pb + O \longrightarrow PbO + \text{high temperature} \qquad (Ia)$$

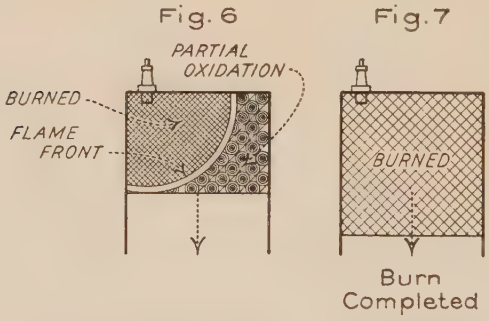
Thus, by virtue of the multiple centers of high temperature created by Reaction I*a*, there is initiated evenly ahead of the main flame front a partial oxidation or an auxiliary burn (Figure 6) tending to maintain normal combustion in a region of fuel which would otherwise be subject to detonation. Figure 7 represents the normal burn completed



Antiknock Present as Vapor

Temperature of Antiknock Approaching Its Decomposition Temperature

Antiknock Has Decomposed, Scattering Pyrophoric Particles through Charge



Oxidation of Antiknock Initiates Oxidation in Otherwise Unburned Gases Ahead of Flame Front Maintaining Normal Combustion

No Detonation of Gases Ahead of Flame Front CO_2, H_2O, PbO

The decomposition temperature of antiknock materials, taken in conjunction with the temperature of the cylinder gases, thus determines at what stage in the cycle they shall begin to function. If the decomposition temperature is low, partial oxidation will begin earlier in the cycle and extend throughout a larger volume of yet unburned fuel than if it is high. In the extreme latter case it would cause a lowering in the efficiency of the compound, while in the

former it might cause slight preignition. (Note action of bismuth alkyls in next section.) The ideal antiknock should possess a decomposition temperature which will cause it to begin to function just with or just after ignition of the charge by the spark plug.

The relative effectiveness of an antiknock compound would be thus determined by the following set of properties, optimum conditions appearing in parentheses:

(1) Volatility (boiling point should be under 400° C.).
(2) Amount of free metal liberated when heated in the air (should be complete).
(3) Decomposition temperature (should be between 200° and 300° C.).
(4) Temperatures developed by oxidation of the metal (should be high compared to ignition temperatures of the fuel).
(5) Size of particles and rate of oxidation (size, colloidal, to favor rapid oxidation; the lower limit of this case is the liberation of a readily oxidizable vapor—e. g., selenium).

Supporting Evidence

The failure of the mercury alkyls to function as antiknock materials may now receive explanation, and is considered strong negative evidence in support of the theory. Although fulfilling conditions (A) and (B) of the theory, they fail to fulfil condition (C)—namely, that the metal be readily oxidizable with the liberation of a relatively large amount of heat. Mercury is quite stable toward oxygen, its oxide being actually *decomposed* at the working temperature of the motor. It would thus be impossible for it to function in the motor as a true antiknock material, since it cannot by virtue of any heat evolved in its own oxidation induce oxidation in the fuel. In this connection it is further predicted that gold, silver, and platinum would not show antiknock properties, for they are all metals stable toward oxygen with low heats of oxidation, that of gold being negative. The negative evidence in the case of these metals bears out the prediction. (Table II)

The failure of such compounds as lead di- and tetrastearate, the corresponding acetates, and lead diphenyl diacetate (Table II) to function as antiknocks is also explained, since the metal is already oxidized within the compound, being in all cases bound to the organic residue through oxygen. Inorganic compounds in general fall into this classification. However, in the compounds lead thioacetate and lead ethyl xanthogenate the lead atom is joined to sulfur. Lead with this bonding has been shown (Table I) to possess antiknock properties, but its effectiveness is only about one-twelfth that of a lead-carbon linkage. From the point of view of the present theory, the grouping $Pb\begin{smallmatrix}S-\\S-\end{smallmatrix}$ is considered as the active antiknock constituent rather than the lead itself. Thermochemical data show that under conditions

of oxidation this group can oxidize to PbO with sufficient facility to exert an antiknock effect.

In Table VII are given heats of combustion of typical compounds of lead and antimony which exhibit and fail to exhibit antiknock properties and these illustrate further how the bonding of the antiknock metal affects its ability to undergo oxidation in the motor. The data were obtained by carrying out oxidations in a Parr combustion calorimeter.

Table VII—Heats of Combustion of Lead and Antimony Compounds and Effect on Knock in Motor

Compound	Formula	Effect on Knock	Heat of combustion of 1 gram mol calories
Lead tetraphenyl	$Pb(C_6H_5)_4$	Suppressor	3480
Lead diphenyl dinitrate	$Pb(C_6H_5)_2(NO_3)_2$	Inert	1340
Lead diphenyl diacetate	$Pb(C_6H_5)_2(C_2H_3O_2)_2$	Inert	1570
Antimony triphenyl	$Sb(C_6H_5)_3$	Suppressor	2220
Antimony triphenyl sulfide	$Sb(C_6H_5)_3S$	Inert	965

It will be noted that the antiknock compounds above possess a heat of combustion several fold greater than that of the related compounds of the same metal which have no effect on the knock. In other words, as already pointed out, when a metal is already oxidized within a compound no antiknock effect may be obtained from it. In the case of such compounds as lead diphenyl dichloride and lead diphenyl dibromide, which exhibit an antiknock effectiveness less than that of lead tetraethyl, this lowering may be accounted for on the basis of a partial internal oxidation arising from the lead-halogen bonding which is sufficient to lower but not destroy the antiknock property.

Similar calorimeter data, if obtained for a large number of compounds whose effect on the knock is known, would be expected to shed considerable light on the present theory.

Probably the most direct piece of evidence in this work that the antiknock material *per se* plays an actual part in causing partial oxidation of the fuel is the unique behavior of the bismuth alkyls. These compounds are particularly sensitive to heat, decomposing at temperatures a little above 100° C. This means that when tested in the motor especially at high compressions, considerable metallic deposition occurs during the compression stroke and before the mixture is fired by the spark plug. Thus, the antiknock would begin to function early in the cycle. The motor test at a 5.3:1 compression showed this to be true, for abnormally high cylinder pressures were registered by the indicator although there was no knock with a fuel which was otherwise subject to violent detonation. This means that the partial oxidation had started before the spark plug had fired and was developing pressures high enough by the time the piston had reached dead center to cause operation of the pressure indicator in the manner observed. A similar behavior for certain tin alkyls has been reported by Boyd.[11] Such compounds thus function in the same general

[11] Private communication.

manner as do other antiknock materials but earlier in the cycle, a circumstance which exaggerates one phase of the mechanism of their action and so tends to make it more directly apparent.

The present theory that the spreading of the oxidation process throughout a large volume tends to decrease detonation is supported by the observation of Dickinson[12] that multiple points of ignition (multiple spark plugs) tend to eliminate the knock. In this case oxidation is taking place at any instant throughout a larger quantity of fuel than would otherwise be the case, and in a manner comparable to the effect produced by antiknock compounds. The antiknock effect is the limit of the multiple spark plug effect and it is felt that the two are mutually consistent.

Aromatic Amines as Antiknock Materials

The antiknock effect of the aromatic amines is considered similar to that of organo-metallic compounds. In this case, however, it is the hydrocarbon radicals attached to the nitrogen atom which oxidize more readily than the fuel itself and so tend to spread and broaden the region of fuel undergoing oxidation at any instant. That the amino nitrogen atom actually imparts an unstable character to such compounds is illustrated by the fact that when α-naphthylamine is oxidized it is the benzene nucleus to which the nitrogen atom is attached that first splits off. The presence of amino nitrogen thus simply serves to impart an unstable character to the compounds whereby their ease and rate of oxidation is materially greater than of simple hydrocarbons. In a series of amino nitrogen compounds with antiknock properties the effectiveness of a given individual would be determined by its stability and the amount of oxidizable hydrocarbon residue (molecular weight) attached to the nitrogen atom. This suggestion may account in part for the variations reported by Boyd[3] in the effectiveness of these compounds as antiknock materials.

Iodine as an Antiknock Material

The action of iodine, elemental and combined, as an antiknock is difficult to explain from the point of view taken here. The element, however, does form unstable oxides and is known to act as an oxygen carrier. If it so behaves, as a true oxidation catalyst facilitating the oxidation process taking place in the cylinder, the mechanism of its action would differ from that of the other antiknock materials already considered, but the final result would tend to be the same. Oxidation would be more evenly distributed throughout the volume of the cylinder in a manner analogous to that caused by organo-metallic antiknock compounds. The fact that relatively large quantities (2 to

[12] Dickinson, *J. Soc. Automotive Eng.*, **8**, 561 (1921).

3 per cent) of iodine are required to suppress detonation is probably significant in explaining its action.

Knock Inducers

The present theory is essentially one attempting to explain the antiknock effect and does not confuse this with the knock-inducing effect of certain elements and compounds. It is not felt in the light of present knowledge that any theory should necessarily at once account for both phenomena, and that, furthermore, there seems no *a priori* reason for believing that the two effects, so far as compounds which produce them are concerned, are mutually related. It has seemed best to avoid confusion by considering, for the present at least, the action of these two classes of compounds as separate and distinct.

Acknowledgment

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AUTOBIOGRAPHY

I, William Hale Charch, was born in Dayton, Ohio, March 20, 1898. I received my elementary and secondary education in the public schools of this city, being graduated from Stivers High School, June, 1915. My undergraduate education was received at Miami University, Oxford, Ohio, from which I obtained the degree of Bachelor of Arts in June, 1920. My post-graduate work was taken at Ohio State University, Columbus, Ohio. I received the degree of Master of Arts from this university in June, 1921, and the degree of Doctor of Philosophy in Chemistry, September, 1923. While in residence at Ohio State University, I acted in the capacities of Graduate Assistant and Assistant during the school years 1920–1921 and 1921–1922, respectively. During the school year, 1922–1923, I held a University Fellowship.